Gold Plating for the Electronics Industry

A REVIEW OF THE FIFTH SYMPOSIUM OF THE AMERICAN ELECTROPLATERS' SOCIETY

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As is usual at the annual meeting of the American Electroplaters' Society, held this year in New York, the session devoted to plating in the electronics industry included a number of papers concerned with the electrodeposition of gold and the properties of the deposits.

Since the discovery of codeposited organic substances and other materials in gold electrodeposits by Gloria Munier in 1969 and the observations of a number of later workers there has been considerable interest in their nature, their dependence on solution parameters and bath operating conditions, and their effect on deposit properties. A paper by Ch. J. Raub, of the Forschungsinstitut für Edelmetalle und Metallchemie in Germany, described the work of his associate A. Knödler on "The Properties of Gold Electrodeposits Containing Carbonaceous Material." The basic electrolyte contained 8 g/l gold as $KAu(CN)_2$, 100 g/l citric acid, and 40 g/l NaOH. Hardeners, when used, were cobalt or nickel as the sulphates. Solutions without metal additions gave nearly pure deposits. Small additions, such as 0.025 g/l cobalt, caused hydrogen evolution during gold plating and a significant decrease in current efficiency, while simultaneously substances containing carbon, nitrogen, oxygen, and hydrogen were codeposited, their amounts increasing with the amount of cobalt or nickel in the deposit. The carbon levelled out at about 0.2 per cent at a hardener value of 0.1–0.2 per cent. At 1 A/dm² and a pH of 3.5, increasing bath temperature decreased the cobalt and carbon values, while with the nickel-containing bath, nickel in the deposit increased with decrease in carbon level. At a pH of 4.5, both cobalt and nickel dropped, while carbon fell less markedly.

Codeposited material caused high tensile stresses which became less with increasing pH (from 3.5 to 4.5), and with increasing temperature. Low stress deposits were semi-bright or dull; bright deposits were highly stressed, even to the extent that they cracked spontaneously when several microns thick.

It is difficult to draw conclusions as to the identity of these codeposited compounds, as can be surmised from the changing ratios of carbon, hydrogen, oxygen and nitrogen in the deposits shown in the table, abbreviated from the paper. In addition to the earlier finding that the hardener is in solid solution in the gold, Raub conjectures that some may be incorporated with potassium in the deposit in complexes such as $K_6Co_2(CN)_{10}$.

Dependence of Codeposited Material on Bath Hardener

(8 g/l Au, 1 A/dm², 30 °C, pH=3.5, citrate buffered)

	Molar Ratio in the Deposits				
Co, g/l	C : Co	C	: H	: O	: N
0.05	4.44	1	3.71	0.25	0.49
0.2	3.80	1	3.27	0.14	0.61
0.5	2.96	1	2.95	0.13	0.60
Ni, g/l	C:Ni	C	: H	: O	: N
0	—	1	4.11	0.49	0.42
0.05	25.78	1	3.34	0.42	0.36
0.2	7.14	1	3.83	0.30	0.38
0.5	3.53	1	3.22	0.21	0.42
1.0	2.25	1	2.75	0.19	0.35
3.0	0.35	1	3.30	0.18	0.67

In a paper on "Polymer in Gold Plate – Some Practical Observations", F. H. Reid, of London, reported a study he made at W. Flühmann AG, Zürich, Switzerland. His objectives were to determine whether a simple, rapid technique could be devised for monitoring polymer level in gold deposits, and whether such information might be useful for control purposes in industrial plating. Polymer was observed with a binocular microscope during the dissolution in 1:1 aqua regia of gold deposits that had been freed from their substrates. With platings at least 5 microns thick it was possible to rate the amount

of polymer residue as "A" negligible, "B" polymer present-discontinuous film, and "C" polymer present-continuous film. Deposit thicknesses must be the same to enable this qualitative distinction to be made. Also, a technique for dissolution, collection in a filter stick, washing, drying, and weighing was used.

With a cyanide-based gold-cadmium-copper alloy which is normally low in polymer level there was no relation between its amount and the ductility, internal stress, or porosity of the deposit. Inadvertent use of excess wetting agent promoted polymer formation, while the addition of make-up $KAu(CN)_2$ also increased polymer level, presumably due to impurities which could be reduced, however, by carbon filtration of the bath.

Using a cobalt hardened acid cyanide gold, pulse (on-off) duty cycles reduced the polymer level and promoted deposit ductility without significant effect on cobalt content, but even "ductile" deposits from this bath contained polymer. In direct current plating, the amount of polymer increased with increase in the amount of cobalt deposited.

Finally, combustion analysis of collected polymer suggested that one-sixth of the cobalt in the gold might be incorporated in it.

Polarisation Studies

J. P. Sandstrom, of Plessey, Los Angeles and P. Watson, of Plessey, Northants, U.K., reported "A Polarisation Study of Alloy Gold Deposition." Their purpose was to explain the effects of changes in plating variables on the cathode efficiency and cobalt content of deposits plated from a typical hard acid cyanide gold. The approach used was to make potentiodynamic polarisation (Tafel) curves by sweeping the potential under potentiostatic control between the working electrode and a counter electrode. Gold sheet was used for the working electrode, platinum sheet for the counter electrode, and potential was controlled with respect to a saturated calomel electrode. Various test solutions were studied, including one containing 8 g/l of gold as $KAu(CN)_2$, 96 g/l KH_2PO_4, 24 g/l citric acid, and cobalt–EDTA brightener at a pH of 4.1.

Data analysis suggests that the cobalt reduction takes place initially from the (+3) to the (+2) oxidation state, then to cobalt metal. Although gold deposition was diffusion controlled, this is not the case for cobalt deposition. Cobalt deposition depends on the gold deposition rate. At the gold content used, codeposition of gold and cobalt does not take place under steady-state conditions unless at least 1.0 g/l of cobalt (+3) is present. Thus, sufficient cobalt (+3) must be available in the cathode diffusion layer to maintain steady state coverage of the electrode with cobalt (+2) so as to assure that as much cobalt metal will be deposited with the freshly formed cobalt (+2) as can be accommodated by the lattice of the depositing gold.

High Speed Plating

G. R. Hower and D. C. Woerner, of Western Electric, Pennsylvania, in their paper "An Application of Velocity Spot Gold Plating Without Masking", examined the selectivity and efficiency of high-speed plating small circular areas on an integrated circuit lead frame. Although this is common practice with jets of plating solution and masks that confine the deposit to the desired areas, selective plating without masks, particularly in non-dc conditions, is less common. In their study of a prototype system, gold plating solution was continuously filtered and recirculated from a reservoir to the part through nozzles. It was found that significant selectivity could be achieved in dc plating by simply positioning the anode close to the target areas with the lead frame outside of the plating solution. With periodic reverse waveforms both spot size and average gold thickness decreased with increasing efficiency, indicating that improved selectivity is gained at the expense of plating efficiency. However, with a 90 per cent duty cycle at 2500 Hz offset equally 9.5 V in the reverse directions, 200 microinches of gold could be deposited in only 15 seconds. Difficulties were encountered with uniformity of deposit thickness in multiple spot plating with individual plating streams served by a manifold; this was not considered inherent in the process, but due to non-uniform solution flow attributable to deficiencies in cell design.

H. Shoushanian and A. M. Weisberg, of Technic, Rhode Island, U.S.A., discussed "Low Carat Silver-Gold Alloy Deposits." They recommend that of the various alloy gold platings, the silver golds from 12 to 18 carat be used with an overplate of nearly pure hard gold consisting of at least 25 per cent of the total thickness. This practice gives about 42 per cent savings in materials costs, calculated for a 14 carat silver-gold with gold at $200 an ounce troy. Silver-golds are preferred to other binary and to ternary alloys because of their generally superior electrical and mechanical properties. Applications include platings for watchcases, flatware, and the contacts of electrical connectors. Disadvantages include the need for extra processing (three gold tanks including a strike bath with associated rinses), and a higher degree of operating control than is customary in most plants compared to that required for conventional high carat deposits. Also, the properties of duplex gold platings on connectors and on printed wiring board contacts, which use most of the electroplated gold in the U.S.A., have not been completely elucidated.